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AIR QUALITY MARATHON

Annual Report, 1978

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Ontario

Ministry of the Environment

AIR QUALITY

MARATHON

Annual Report, 1978

TECHNICAL SUPPORT SECTION
NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT

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CONTENTS

SUMMARY

Air quality investigations in Marathon, begun in 1974 by the Ontario Ministry of the Environment, continued in 1978 with vegetation and soil studies, snow sampling, and air quality monitoring.

There was no evidence in 1978 of sulphur dioxide injury to vegetation near a local kraft pulp mill. Sulphur dioxide damage was last noted in 1976.

Concentrations of mercury in 1978 decreased sharply in vegetation, experimentally exposed moss, and in snow near the mill following closure of the mill's mercury-cell chlor-alkali plant in August, 1977. Mercury also declined substantially in subsurface soil (5-15 cm in depth) in the same area but remained at high levels in surface soil. Mercury contamination in soil also persisted in a small area near the mill's effluent outfall on Lake Superior and near a company-owned warehouse. Mercury levels in vegetation and soil in the town area were normal.

Vegetation, soil and snow sampling demonstrated that particulate fallout continued to be excessive just south of the mill. Calcium, carbon, chloride, sodium and sulphate were identified as important components of particulate matter deposited in this area. None of these contaminants were found at significant levels in the town.

Dustfall measurements indicated that re-entrained road dust was more significant than mill emissions as a contributor to dustfall in Marathon.

Sulphation rate measurements revealed that significant concentrations of sulphur-containing pollutants were sometimes present in Marathon residential areas. This finding was confirmed by a mobile monitoring survey in late 1977 which showed that total reduced sulphur (TRS), responsible for offensive odours, frequently exceeded the Ontario guideline in the town and on Highway 17. The completion of a major mill modernization programme in early 1979 is expected to result in major reductions in odour and particulate emissions. Continued monitoring is planned to document the effects of these improvements.

INTRODUCTION

The Ministry's air quality assessment programme began in Marathon in 1974. Results of studies up to 1977, released in a series of annual reports (1, 2, 3), demonstrated the occurrence of periodic sulphur dioxide injury to vegetation, and elevated levels of mercury and particulate matter near a local bleached kraft pulp mill and adjacent chlor-alkali plant. In the nearby town area, particulate fallout from the mill was not considered significant, although there was evidence of undesirable high levels of malodorous pollutants from mill emissions.

Investigations in 1978 included further vegetation, moss and soil studies, snow sampling, and the continuation of dustfall and sulphation rate measurements.

VEGETATION AND SOIL ASSESSMENT

VEGETATION

Vegetation around the pulp mill was inspected twice during the 1978 growing season and no evidence of visible sulphur dioxide injury was observed. The absence of sulphur dioxide damage marked the second consecutive year that local vegetation was free of injury symptoms caused by this pollutant.

Triplicate samples of cow parsnip (*Heracleum lanatum*), a local weed, were obtained from 12 sites near the mill (Figure 1) and at two control locations. Sampling and sample processing procedures were the same as those described for earlier studies (2). Collected material was analysed for chloride, mercury, sodium and sulphur at the Ministry's Thunder Bay and Toronto laboratories.

Cow parsnip plants at sites closest to the mill were stunted and lacking flowers in comparison to plants at the most distant sampling points. Foliage of specimens nearest the mill also

sustained moderate to severe marginal necrosis and bore a conspicuous deposit of whitish particulate matter. The concentrations of chloride, sodium and sulphur in cow parsnip, plotted in Figures 2, 4 and 5, were significantly elevated south of the mill. Similar distribution patterns were found for the same contaminants in moss and snow. As expected following the closure of the mercury-cell chlor-alkali plant, there was a very significant decrease in mercury (Figure 3), as illustrated by the data in Table 1.

MOSS

Small quantities of *Sphagnum* moss were set out on June 21 at 15 locations around the mill (Figure 6) to monitor the presence of airborne pollutants. Details of the technique are described in the 1977 report (3). Following a 37-day exposure period, the concentrations and distribution patterns of calcium, chloride and sodium in the moss were very similar to those reported for 1976 and 1977 (2,3) but mercury, as expected, showed a sharp decline (Table 2).

SOIL

Three soil surveys, using standard sampling methods (3), were conducted in 1978 as follow-up studies to similar work undertaken earlier. The principal investigation was a 15-site survey near the mill (Figure 7) where three depths of soil were sampled for mercury analysis in the Ministry's Thunder Bay laboratory. The data, in Table 3, show no significant difference between 1976 and 1978 in the mercury content of surface soil, a moderate decrease in mercury in the 5-10 cm (centimetre) soil layer, and a very large reduction in mercury in the 10-15 cm layer. The distribution pattern of mercury in soil near the mill was similar to that for 1976 (2).

Investigations in 1975, 1976 and 1977 revealed the presence of a small area near the mill's effluent outfall on Lake Superior where mercury concentrations in surface soil were unusually high

(3). In 1978, seven additional sites in the area were sampled. Analysis for mercury showed that significant contamination was present at 5 of the 7 new locations tested (Figure 8). Several shallow excavations (about 5 metres square and 1 metre deep) are present in the area but soil at the bottom of these holes contained less mercury than soil outside the holes. The source of contamination has not been determined, nor has the full extent of the area affected. The implications of the presence of this mercury are unknown. Toxicity to plant life is not suspected, but some of the mercury might enter Lake Superior via groundwater.

A soil survey was also repeated near a storage yard about 1400 metres from the mill. Mercury levels in 1978 in surface soil here (Figure 9) were found to be moderately elevated and about the same as those in previous years. Spillage or leakage from mercury-laden waste stored in drums in the yard is suspected as the contamination source. Since the area involved is very small and mercury concentrations only moderately elevated, this situation is not considered a problem.

SNOW SAMPLING

Core samples of the total snow profile were sampled by the normal procedure (2) from 20 sites near the pulp mill (Figure 10) in January, 1978. Determinations of calcium, carbon, chloride, mercury, sodium, sulphate and pH in meltwater from the samples were made in the Ministry's Thunder Bay laboratory.

The chemical analysis results, in Table 4, show that concentrations and distribution patterns for all parameters except mercury were about the same in 1976 and 1978. The decrease in mercury levels (Figures 11a and 11b) was of about the same magnitude as that found later in the year in moss and vegetation. Mercury in snow near the mill and near the storage yard 1400 metres to the northeast continued, however, to exceed the contaminant guideline.

Visible brown and black particulate matter was conspicuous in snow to the south of the mill and was evident to some extent as far as the residential area nearest the mill. However, all our studies indicate that the bulk of particulate fallout from mill emissions is restricted to company property close to the mill.

AIR QUALITY MONITORING

DUSTFALL

Dustfall, comprising particulate matter which settles out of the atmosphere by gravity, has been monitored in Marathon since mid-1974. The method of measurement is briefly described in the 1977 report (3). Of the four original monitoring sites, three were still in operation at the end of 1978. The equipment at station 63028 was transferred to a new location (63033) at the end of July (Figure 12). Total dustfall determinations and analyses of soluble calcium, chloride, sodium and sulphate in dustfall were carried out by the Ministry's Thunder Bay laboratory.

The data for 1978 (Table 5) reveal a number of values above the Ontario air quality objective for monthly dustfall. Many of the high readings were attributed to re-entrained road dust and not to emissions from the mill. Levels of calcium, chloride, sodium and sulphate in dustfall were at or near background values. Average dustfall, which was similar to that for 1977, was not related to distance or direction from the mill (Figure 13). Black particulate matter was occasionally seen in some of the dustfall jars.

SULPHATION RATES

Monthly sulphation rates provide a semi-quantitative measure of average levels of sulphur-containing gases in the atmosphere. The method is based on the reaction between sulphur compounds and lead dioxide to form lead sulphate. Readings may be obtained in

the presence of any reactive compound (e.g., sulphur dioxide and hydrogen sulphide). Variations in temperature, wind and humidity will also affect results. Despite these limitations, sulphation rates indicate whether average sulphur levels are significant, and may also be useful in determining long-term trends.

The data for Marathon in 1978 (Table 5) show that some very high readings were obtained on company property near the mill (station 63031). Lower, but still significant values, were recorded at locations in the town. The presence of a gradient of decreasing sulphation rates with increasing distance from the mill (Figure 14) indicates that the latter was a source of sulphur-containing pollutants. Comparison with data from previous years (Table 6), suggests a trend of increasing sulphation rates over the past 4 years. The consistently low values for Heron Bay indicate that airborne sulphur pollutants did not exceed acceptable levels during the year at that location.

MOBILE MONITORING SURVEY

In late 1977, a brief air quality survey with mobile monitoring equipment was conducted by the Ministry's Air Resources Branch (4). Measurements were made of total reduced sulphur (TRS), sulphur dioxide and nitrogen oxides.

From the limited data collected, concentrations of sulphur dioxide and nitrogen oxides were found to be generally satisfactory. However, TRS, a group of sulphur-containing gases responsible for offensive odours near kraft pulp mills, exceeded the Ministry guideline for half the survey period. Highest TRS levels occurred near the mill. Concentrations of lesser magnitude, but still well above the guideline, were reported in the town's residential area and as far as Highway 17. Conditions were not favourable for monitoring at Heron Bay.

Since the time of the 1977 survey, the mill has completed a major modernization programme, including a new recovery furnace and a taller stack. These improvements should significantly

reduce community odour levels and also decrease particulate fallout near the mill. Continued monitoring with fixed and mobile equipment is proposed to document the benefits of these developments.

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1. Griffin, H. D. 1976. Air quality, Marathon. Annual Report, 1975. Ontario Ministry of the Environment.

2. Ontario Ministry of the Environment. 1977. Air quality, Marathon. Annual Report, 1976.

3. Ontario Ministry of the Environment. 1978. Air quality, Marathon. Annual Report, 1977.

4. Ontario Ministry of the Environment. 1979. Report on an ambient air survey in Marathon, Ontario, September and October, 1977. ARB-TDA Report No. 52-78.

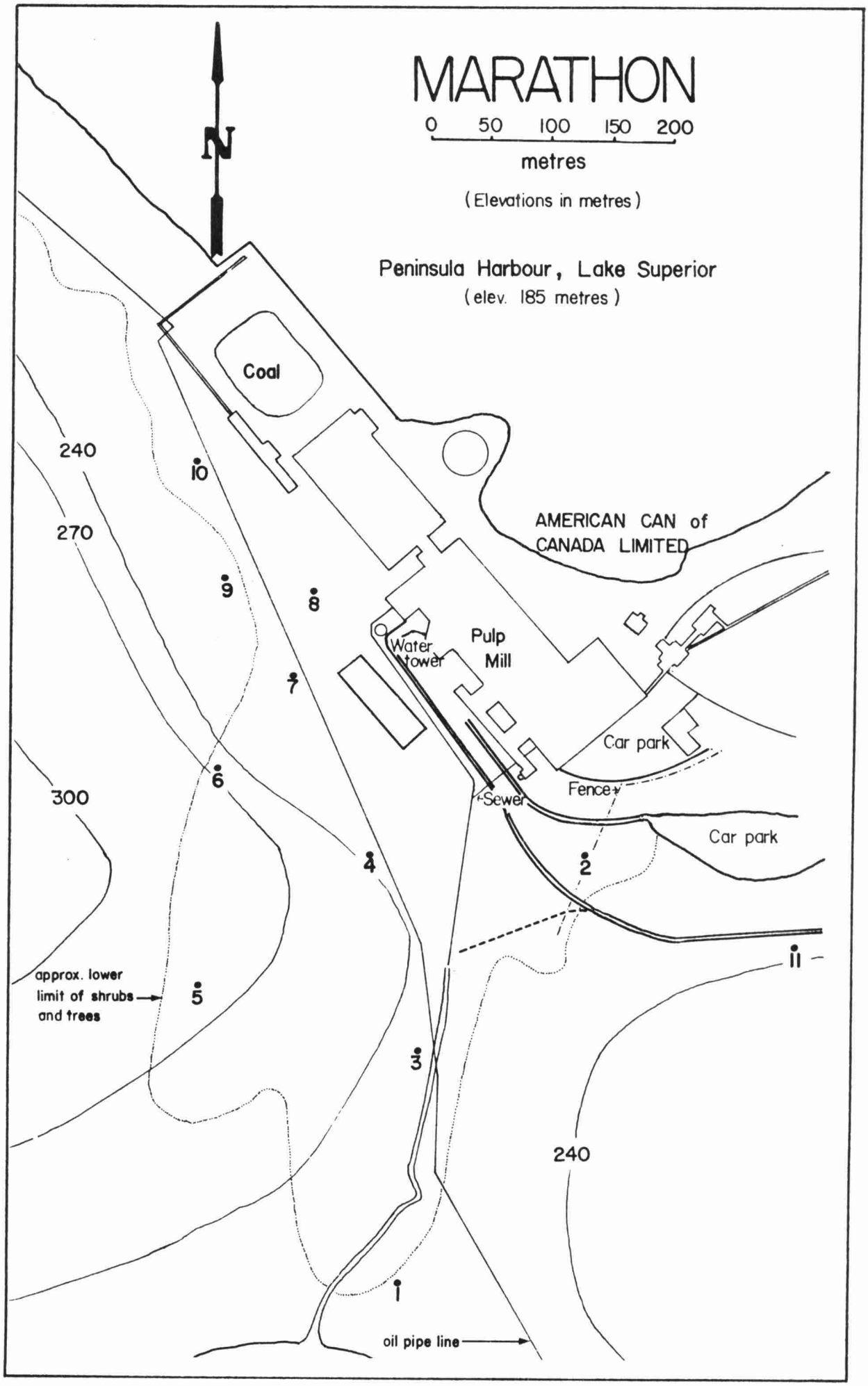

Figure 1. Vegetation sampling sites, 1978.

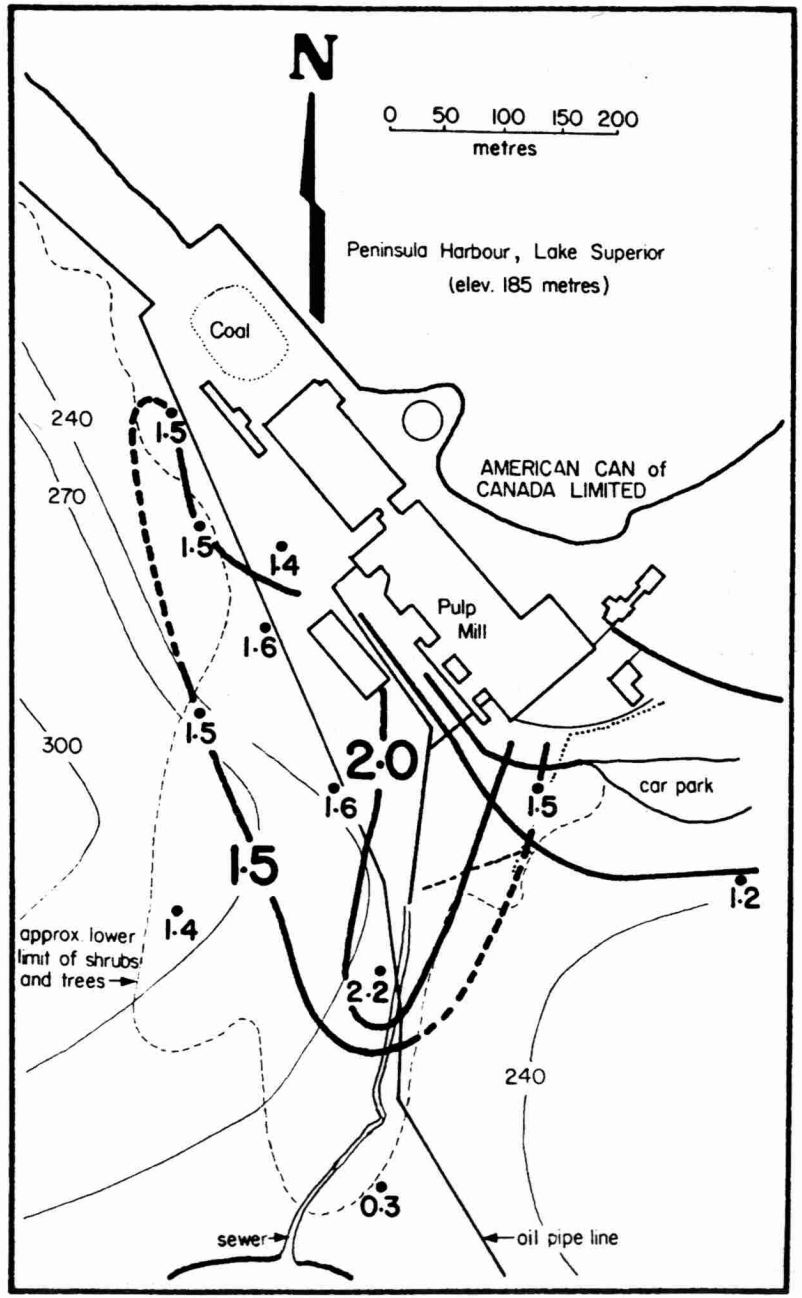

Figure 2. Average chloride content (%, dry weight) in unwashed cow parsnip, July, 1978.

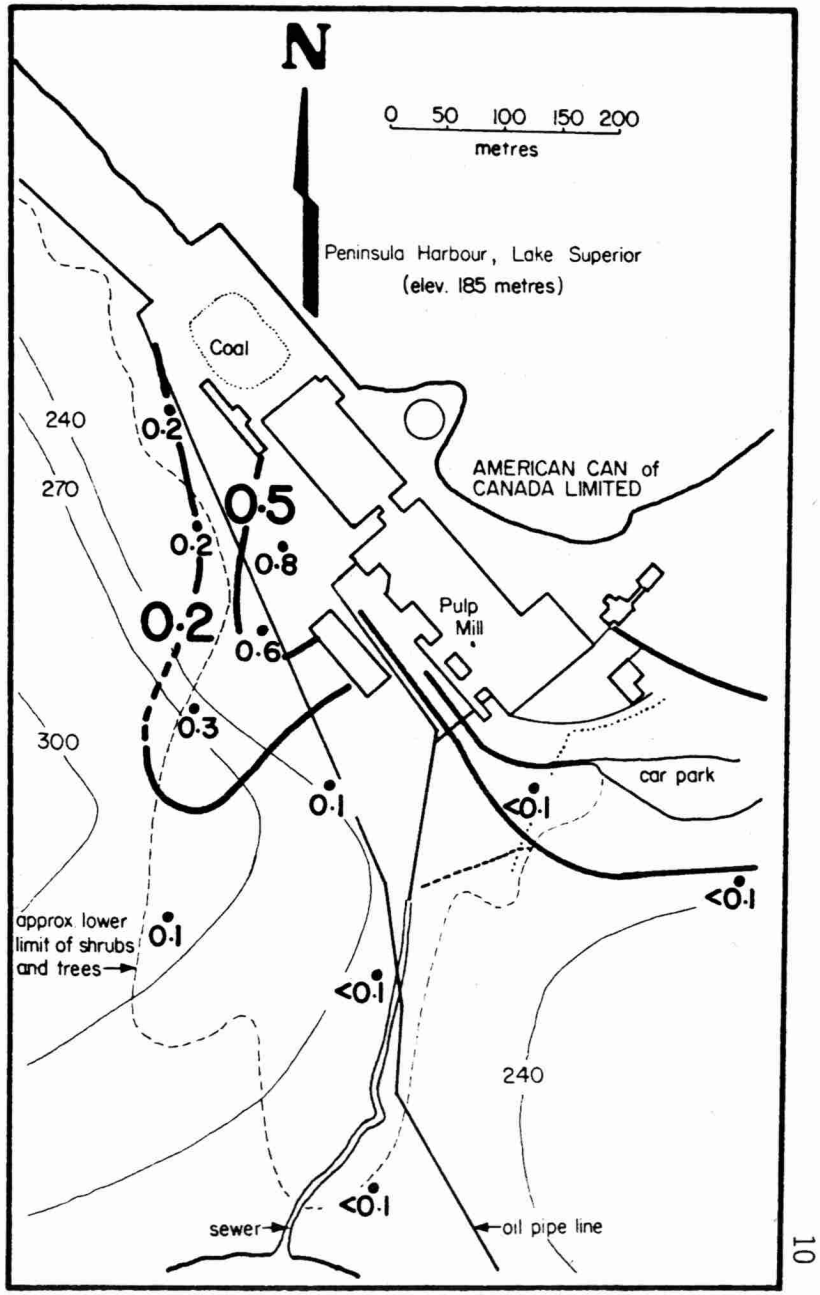

Figure 3. Average mercury content (µg/g, dry weight) in unwashed cow parsnip, July, 1978.

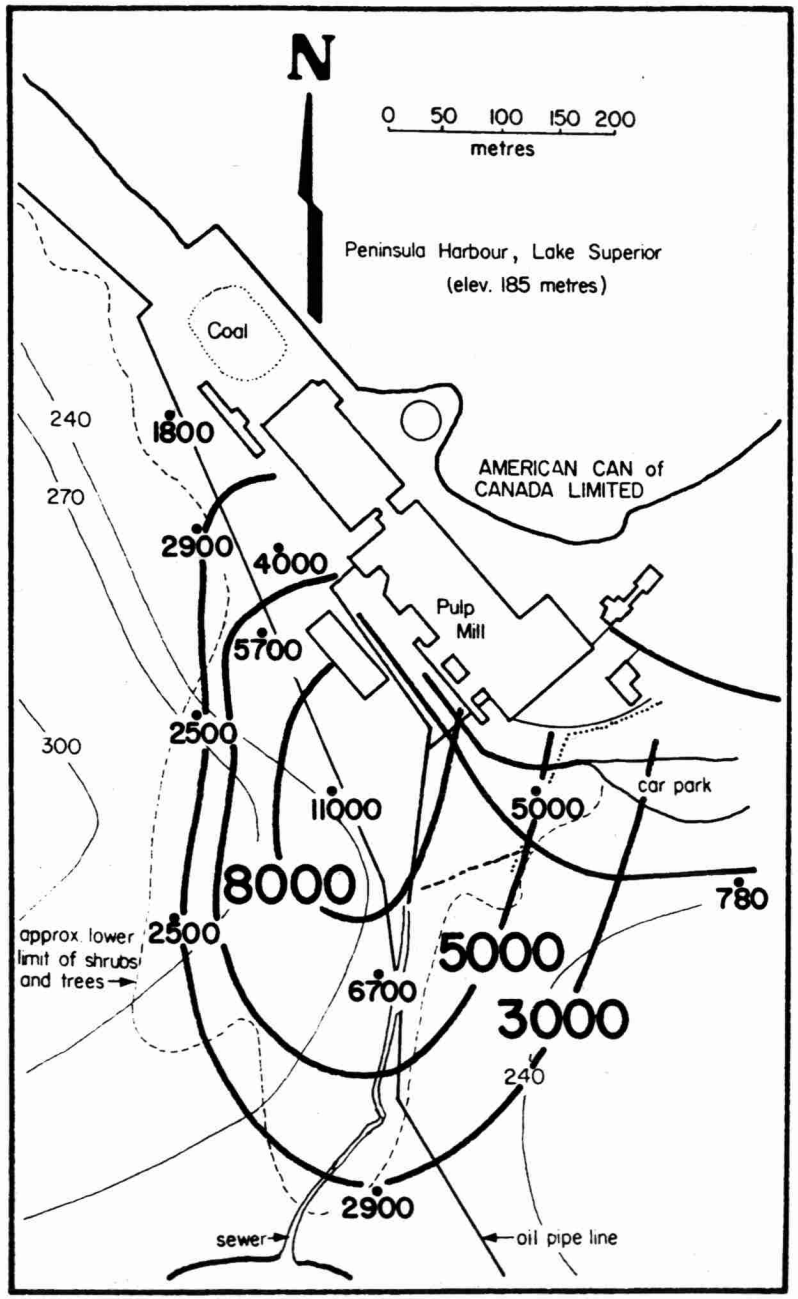

Figure 4. Average sodium content (µg/g, dry weight) in unwashed cow parsnip, July, 1978.

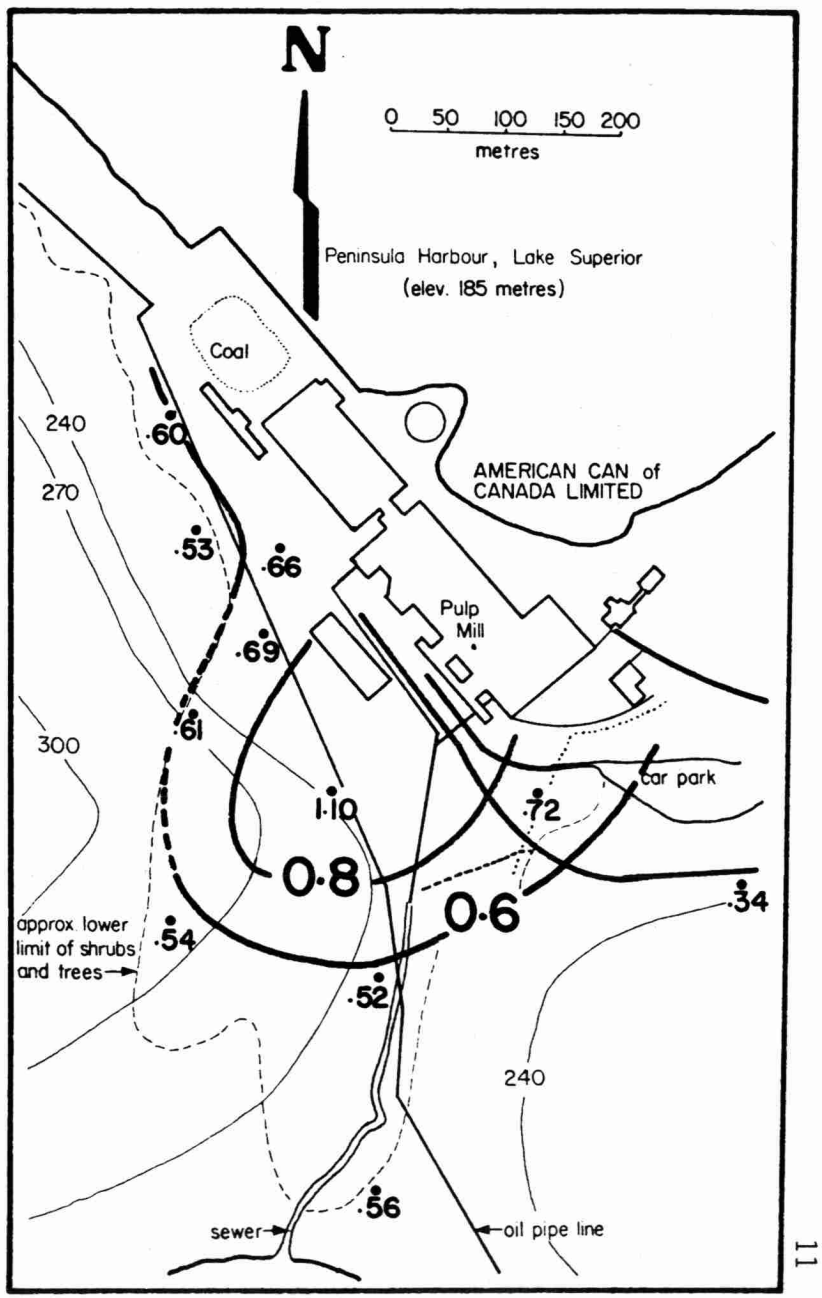

Figure 5. Average sulphur content (%, dry weight) in unwashed cow parsnip, July, 1978.

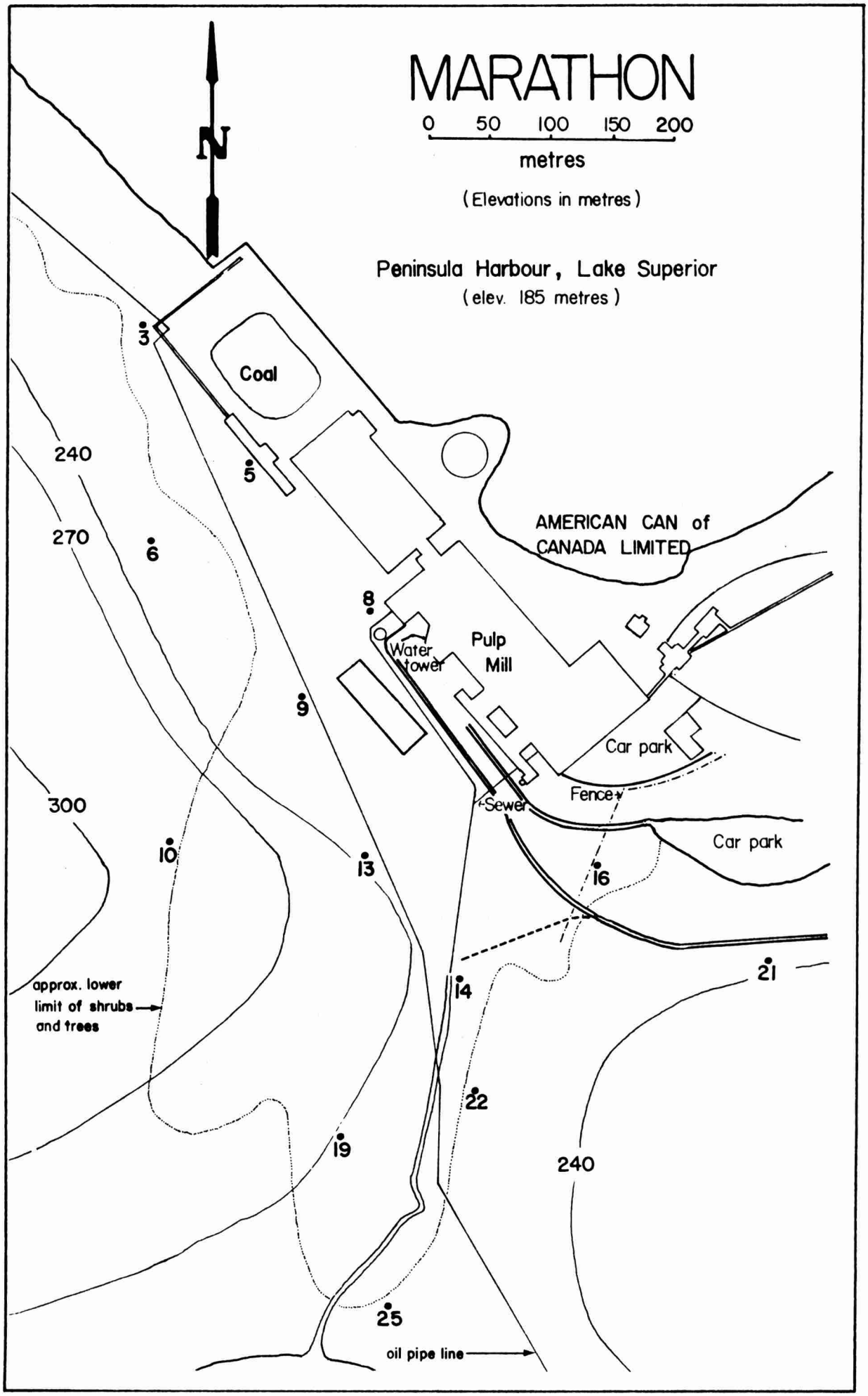

Figure 6. Moss bag exposure sites, 1978.

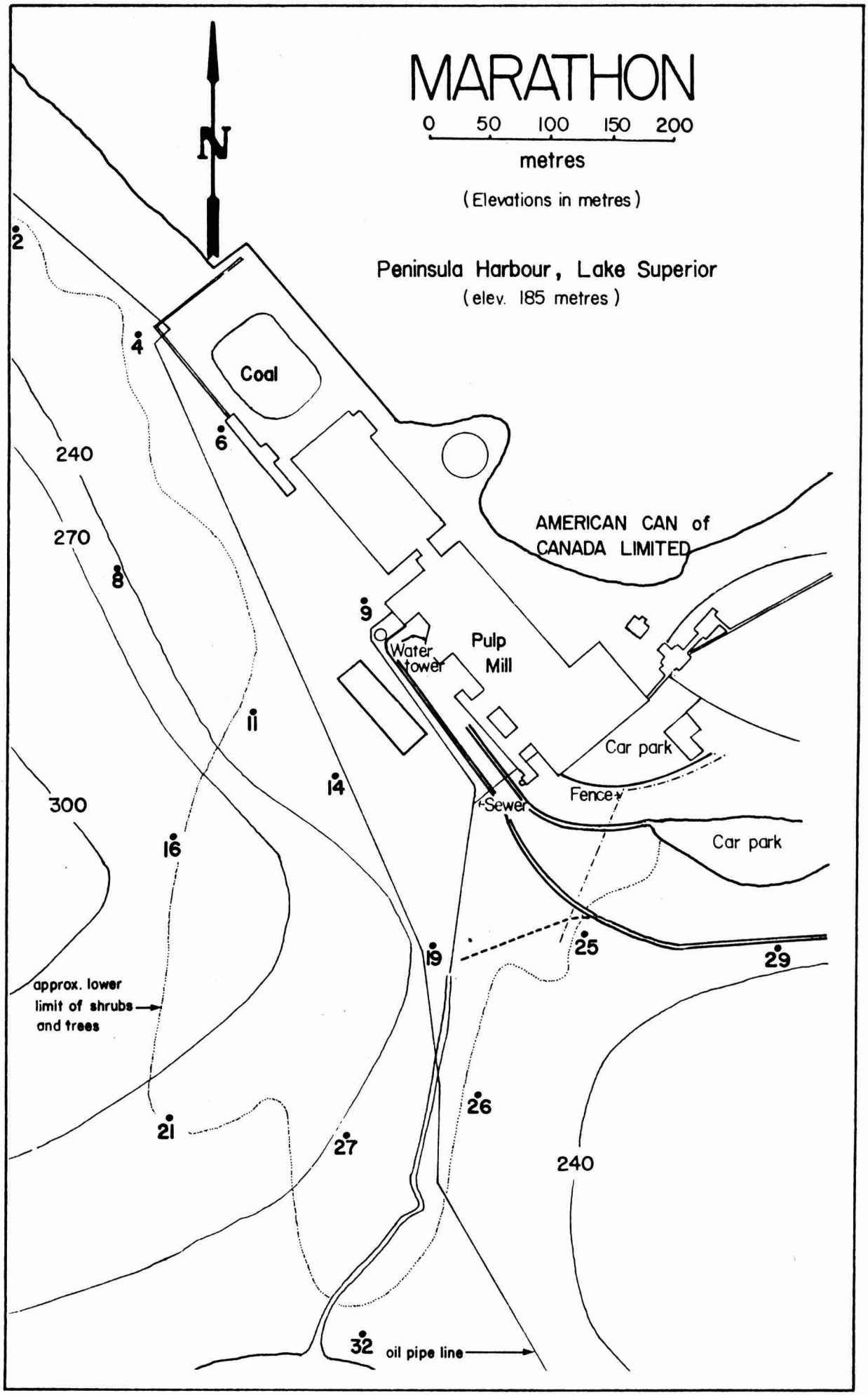

Figure 7. Soil sampling sites, 1978.

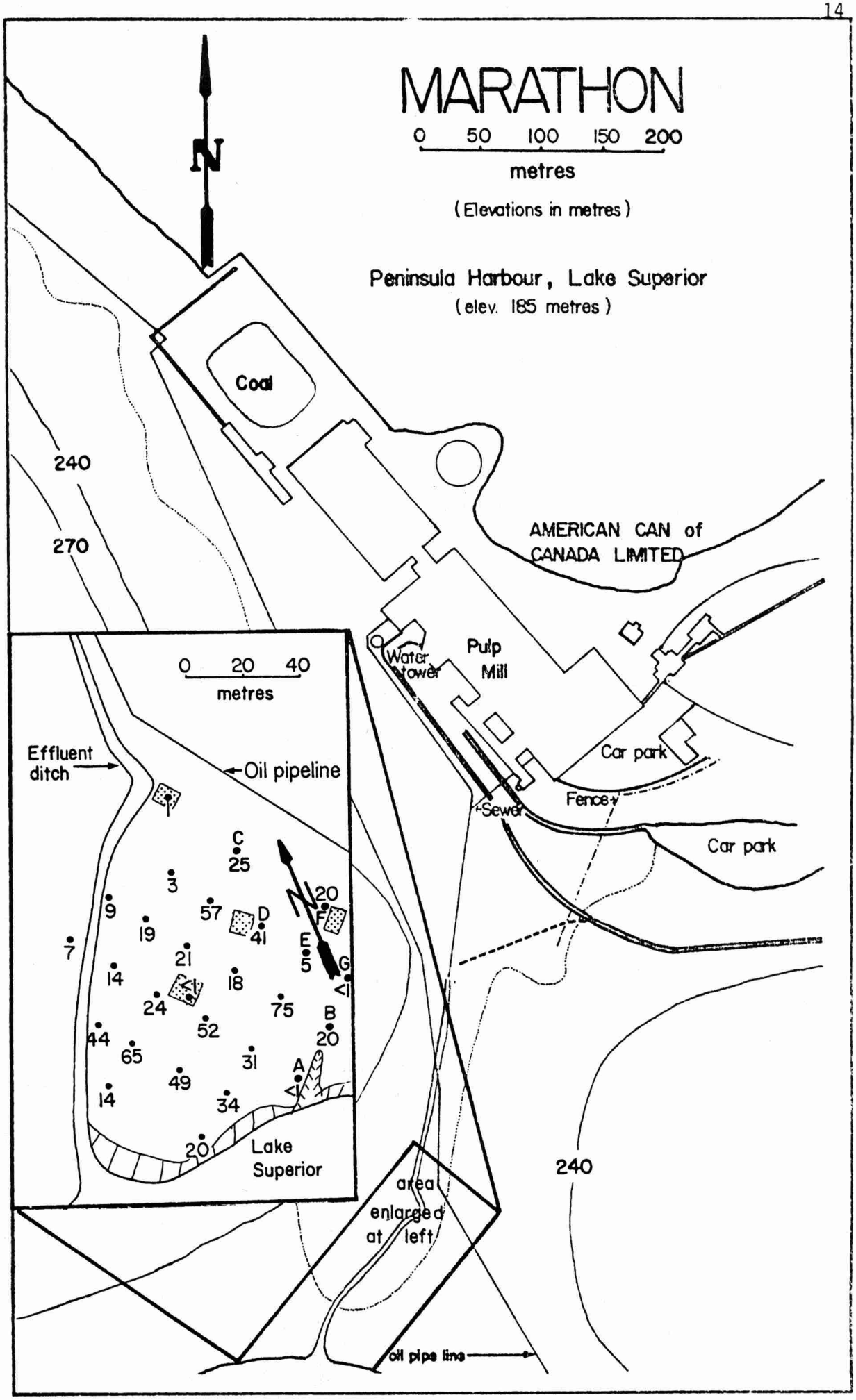

Figure 8. Mercury concentrations (µg/g, dry weight) in surface soil (0-5 cm) near effluent ditch outfall, Lake Superior. Sites A-G sampled in 1978, other sites sampled in 1976 and 1977. ▨ man-made excavations

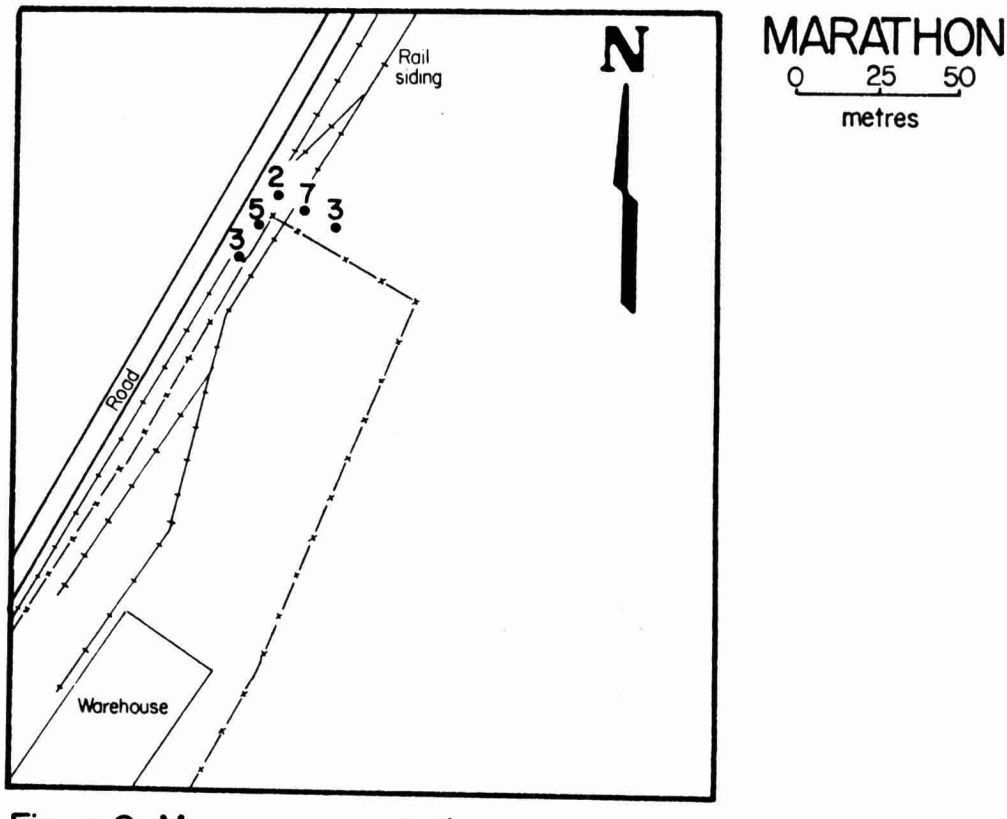

Figure 9. Mercury concentrations (µg/g, dry weight) in surface soil (0-5 cm) near American Can storage yard, June, 1978.

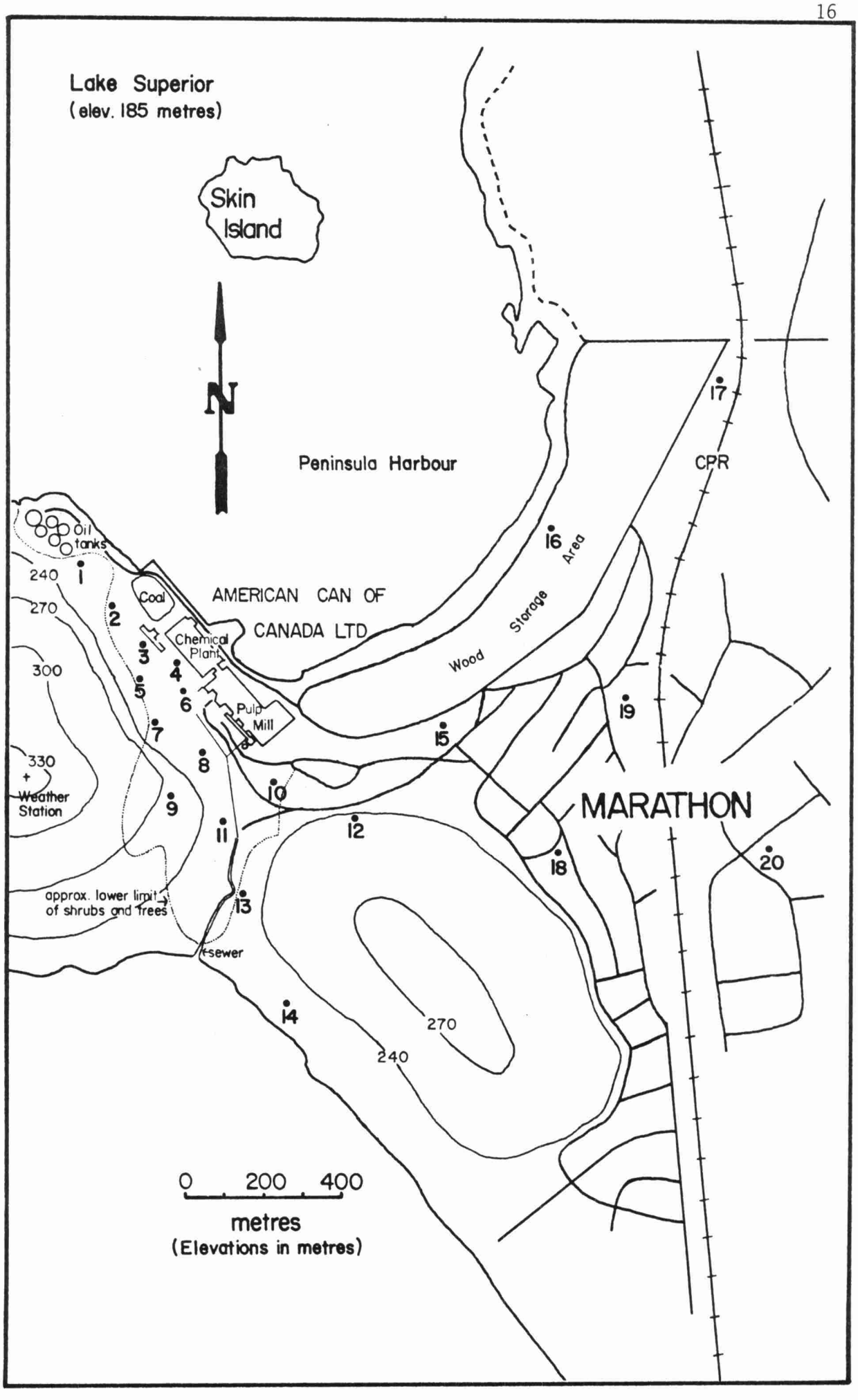

Figure 10. Snow sampling sites, January, 1978.

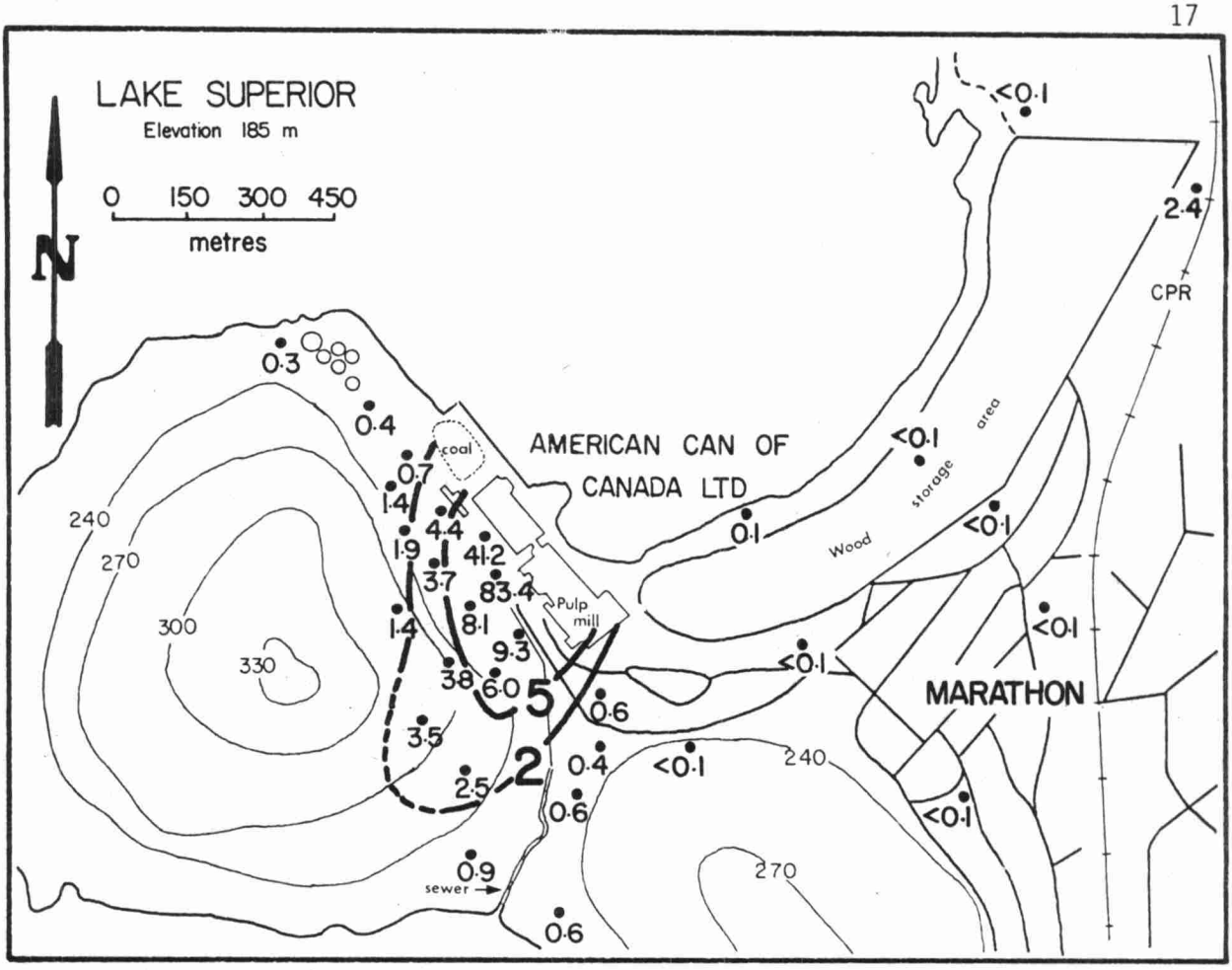

Figure IIa. Average mercury levels (µg/l) in snow, January - March, 1976.

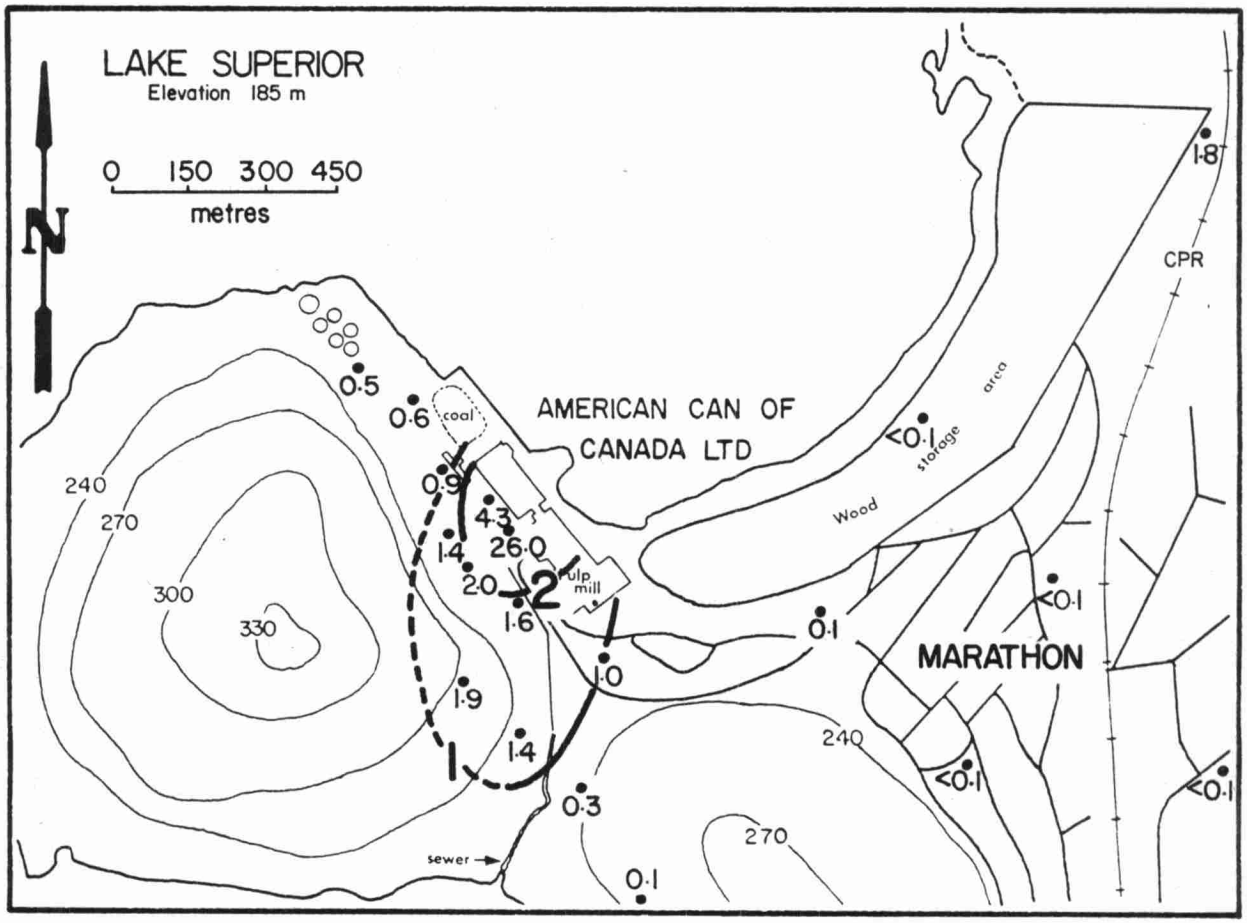

Figure IIb. Mercury levels (µg/l) in snow, January, 1978.

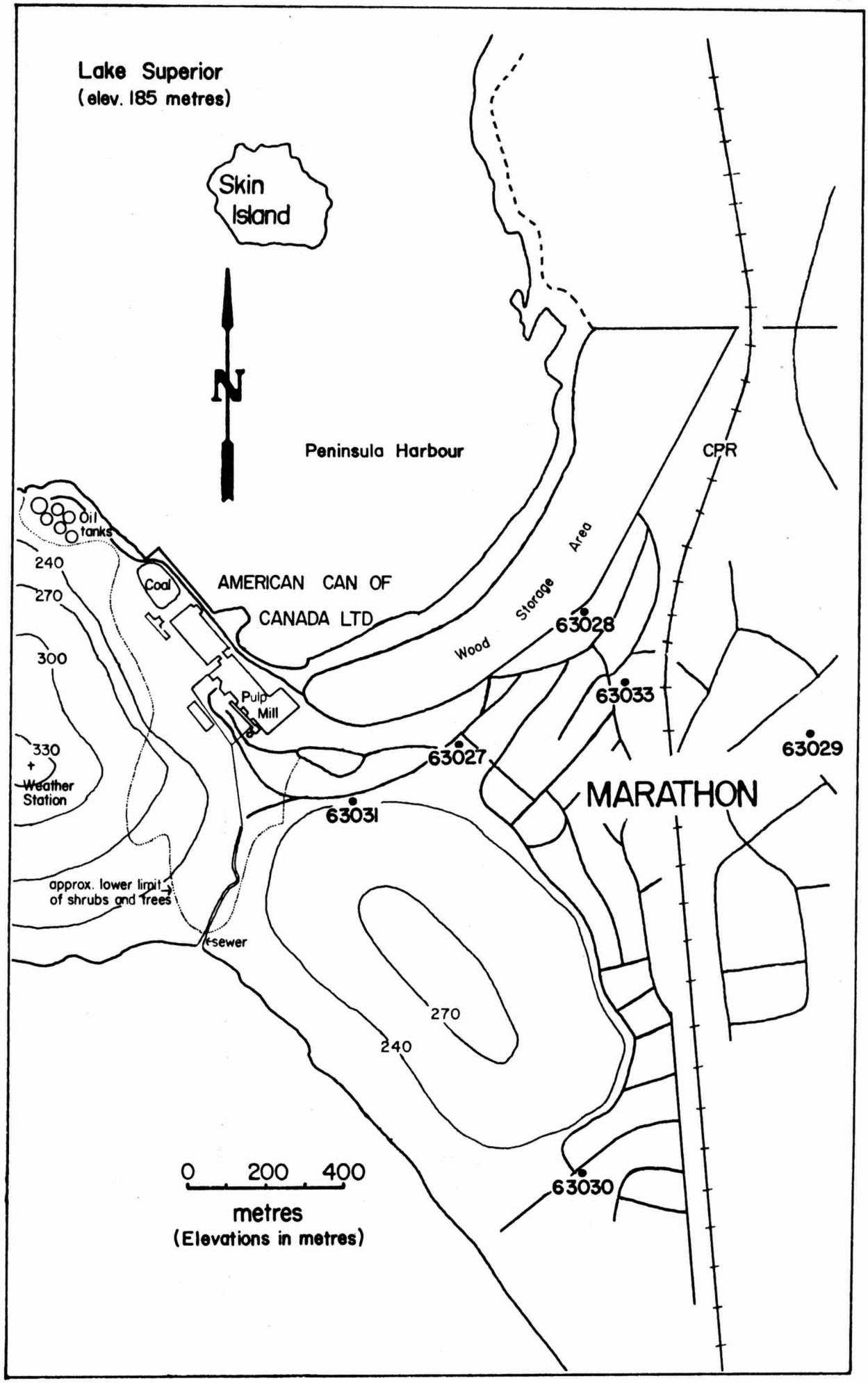

Figure 12. Air quality monitoring sites, 1978 (except station 63032, Heron Bay).

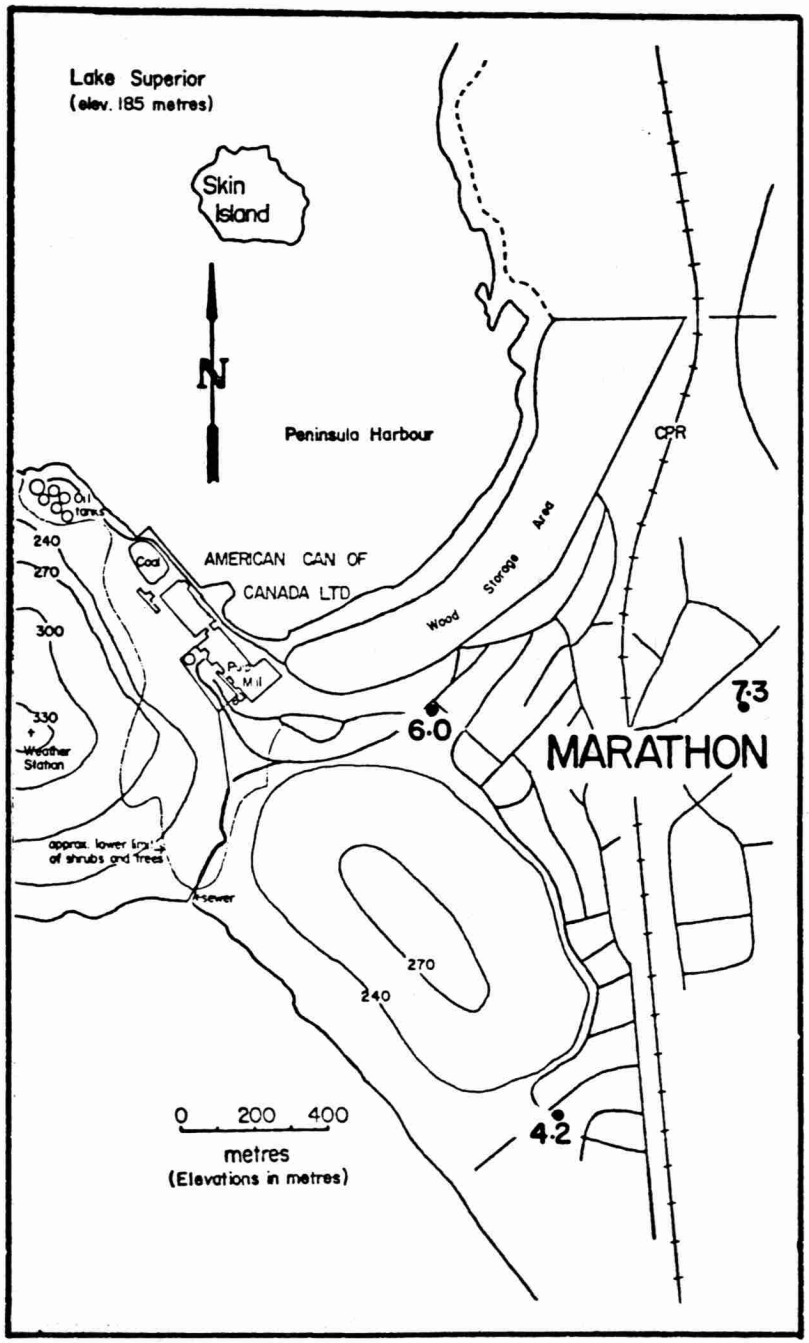

Figure 13. Average dustfall (g/m^2/30 days), 1978.

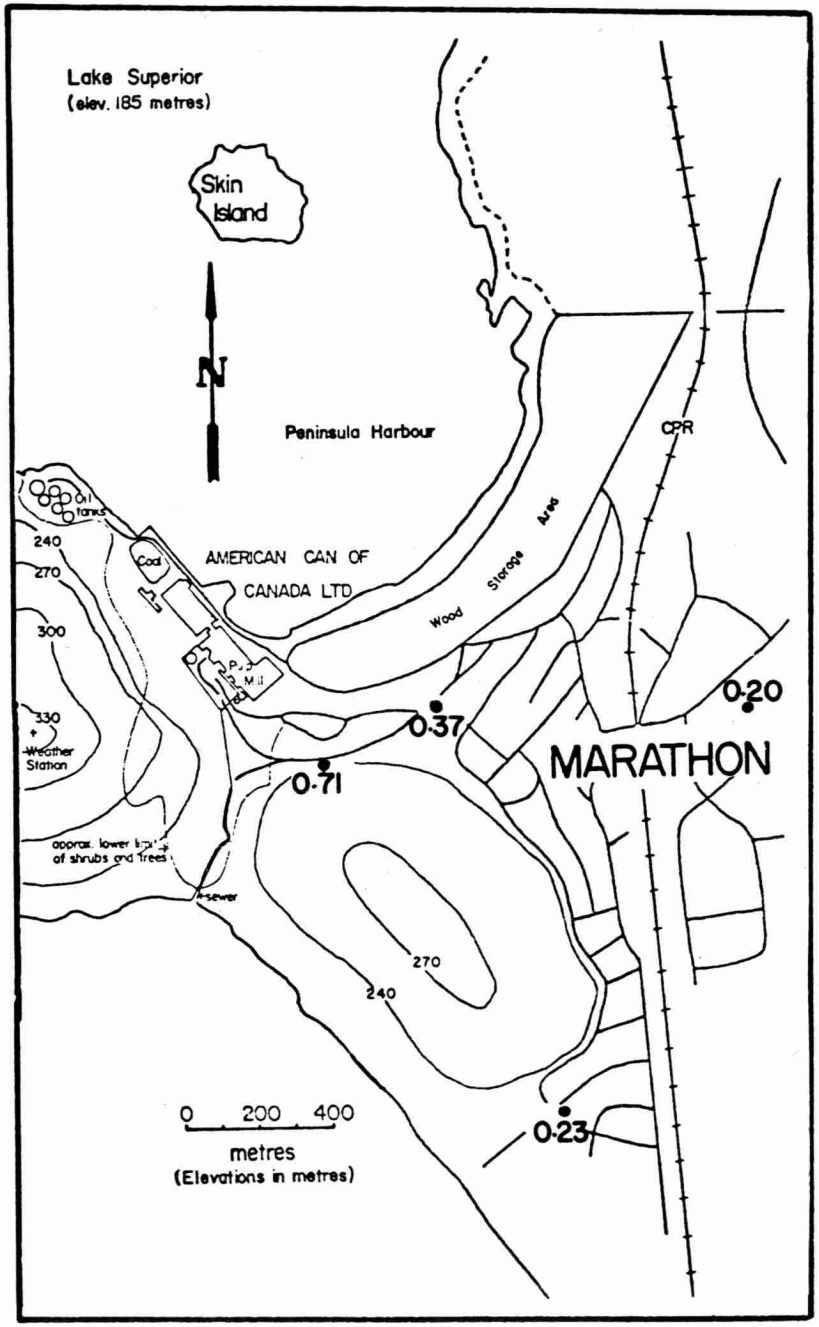

Figure 14. Average sulphation rate (mg SO_3/100 cm^2/ day) 1978.

TABLE 1. Comparison between mercury concentrations in unwashed cow parsnip sampled before and after closure of the chlor-alkali plant.

Sampling site[a] (from Figure 1)	Mercury levels (µg/g, dry weight)	
	July, 1976	July, 1978
2	7.6	<0.1
3	0.9	<0.1
4	2.0	0.1
8	26.0	0.8
9	2.1	0.2
10	1.3	0.2
Controls	<0.1	<0.1

[a]Locations of some sampling sites differed slightly in 1976 and 1978.

TABLE 2. Comparison between mercury concentrations in *Sphagnum* moss exposed before and after closure of the chlor-alkali plant.

Sampling site[a] (from Figure 6)	Mercury (µg/g, dry weight)	
	June 29 to August 19, 1977	June 21 to July 27, 1978
3	3.1	0.4
5	3.5	0.4
6	0.8	0.1
8	180.0	5.4
9	4.6	0.5
10	0.9	0.4
13	8.9	0.4
14	1.3	0.2
16	0.5	0.1
19	0.4	0.2
21	0.2	0.1
22	0.3	0.1
25	0.3	0.1

[a]Locations of some sampling sites differed slightly in 1977 and 1978.

TABLE 3. Comparison between mercury levels, in μg/g, dry weight, in soils sampled in 1976 and 1978 near the American Can chlor-alkali plant.

Sampling site[a] (from Figure 7)	Soil depth					
	0-5 cm		5-10 cm		10-15 cm	
	1976	1978	1976	1978	1976	1978
2	3.6	5.0	2.9	2.1	2.9	
4	7.3	5.0	7.0	8.0	4.0	7.5
6	14.0	18.0	11.0	2.1	5.9	0.9
8	3.1	5.4	5.2	0.8	0.8	
9	36.0	58.0	32.0	13.0	21.0	2.8
11	8.8	9.8	7.0	4.8	3.6	
14	18.0	12.0	14.0	4.4	13.0	2.3
16	2.9	3.3	2.4	0.4	0.4	0.1
19	1.7	1.5	2.0	0.7	1.7	0.2
21	2.8	2.9	1.6	1.0	0.6	0.3
25	1.5	1.5	1.3	0.5	0.6	0.2
26	2.4	2.3	1.4	0.9	0.8	0.5
27	1.4	1.3	0.9	0.4	0.5	
29	0.8	0.6	0.7	0.5	0.2	0.2
32	48.0	43.0	22.0	16.0	6.1	3.6
Controls	<0.1	0.1	<0.1	<0.1	<0.1	<0.1

[a]Locations of some sampling sites differed slightly in 1976 and 1978.

TABLE 4. Comparison between average levels[a] of calcium, carbon, chloride, mercury, sodium and sulphate in meltwater from snow sampled in 1976 and in January, 1978, in Marathon.

Site	Calcium		Carbon		Chloride		Mercury		Sodium		Sulphate	
	1976	1978	1976	1978	1976	1978	1976	1978	1976	1978	1976	1978
1	4	4	4	7	6	8	0.4	0.5	45	9	8	11
2	6	6	5	18	10	12	0.7	0.6	28	20	46	34
3	14	8	7	20	14	22	4.4	0.9	23	33	40	52
4	13	10	20	30	6	22	41.0	4.3	10	62	22	82
5	19	14	-	35	6	12	3.7	1.4	47	54	92	94
6	26	15	37	42	7	29	83.0	26.0	34	120	68	140
7	-	16	-	22	-	13	-	2.0	-	56	-	100
8	37	190	57	25	14	137	6.0	1.6	72	120	168	200
9	-	58	-	22	-	18	-	1.9	-	59	-	150
10	22	30	52	59	4	12	0.6	1.0	68	82	130	170
11	-	42	-	34	-	15	-	1.4	-	32	-	66
12	8	8	9	24	2	2		0.1	20	26	56	63
13	-	25	-	26	-	10	-	0.3	-	28	-	65
14	-	10	-	18	-	2	-	0.1	-	12	-	30
15	3	2	14	19	1	2	<0.1	0.1	8	11	18	18
16	1	4	4	10	<1	1	<0.1	<0.1	1	2	4	4
17	4	2	4	7	2	4	3.3	1.8	2	3	4	5
18	2	2	1	8	12	1	<0.1	<0.1	12	4	12	8
19	1	2	2	6	2	1	<0.1	<0.1	2	2	5	2
20	-	2	-	7	-	1	-	<0.1	-	3	-	6
Controls	<1	1	<1	2	<1	<1	<0.1	<0.1	2	<1	2	1
Guideline	5		10		5		0.5		5		5	

[a]Values for mercury in µg/l. All other values in mg/l.

TABLE 5. Dustfall and sulphation rates, Marathon, 1978.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
			Dustfall (g/m^2/30 days)												
63027	McLeod/Abrams	590 ESE	-	3.6	5.0	8.1[b]	12.3	8.4	10.4	4.2	4.9	3.2	3.6	2.5	6.0
63028	Winton/Stevens	875 E	1.5	2.8	7.1	6.8	21.5	19.7	15.6						
63029	Marathon Shell	1390 E	0.5	1.3	3.0	9.0	15.6	9.9	14.0	9.3	6.6	7.3	9.2	2.1	7.3
63030	Howe/Yawkey	1390 SE	0.6	-	3.2	6.4	4.9	9.0	6.2	2.6	4.2	2.0	2.6	4.4	4.2
63033	Water Tower	1080 E								3.8	4.4	1.5	2.6	0.8	
			Sulphation rates (mg SO_3/100 cm^2/day)												
63027	McLeod/Abrams	590 ESE	.31	.35	-	.71	.22	.32	.12	.20	.24	-	.61	.62	.37
63028	Winton/Stevens	875 E	.26	.22	-	.43	.24	.54	.17						
63029	Marathon Shell	1390 E	.29	.21	-	.22	.16	.31	.07	.18	.18	-	.19	.19	.20
63030	Howe/Yawkey	1390 SE	.36	.35	-	.23	-	.15	.17	.11	.12	.22	.22	.29	.23
63031	Bark Press Road	420 SE	.49	.77	-	.69	.33	.18	.41	.16	.26	1.05	1.35	2.12	.71
63032	Heron Bay	14000 SE	.13	.06	.09	.10	.14	.11	.05	.09	.07	.12	.07	.15	.10
63033	Water Tower	1080 E								.27	.23	-	.31	.35	

[b] Values exceeding maximum acceptable levels of 7.0 (monthly) or 4.6 (annual average) are underlined.

[a] Source arbitrarily designated as recovery furnace stacks, American Can of Canada Limited kraft pulp mill.

TABLE 6. Comparison between average annual sulphation rates (mg SO_3/100 cm^2/day) in Marathon, 1975 to 1978.

Station	1975	1976	1977	1978
63027	.07	.22	.27	.37
63028	.07	.14	.17	
63029	.06	.15	.17	.20
63030	.09	.18	.23	.23
63031		.46	.56	.71
63032				.10

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